




**New dithia-anthracene derivatives and fungicidal compositions containing them**

**Patent number:** GB857383  
**Publication date:** 1960-12-29  
**Inventor:**  
**Applicant:** MERCK AG E  
**Classification:**  
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 CH35 1791 (A)

**Abstract of GB857383**

The invention comprises 2, 3-dicyano-1, 4-dithia anthra quinone and the corresponding hydro quinone. The anthraquinone is prepared by reacting a 2, 3-dihalo-1, 4-naphthaquinone with the di-sodium salt of 1, 2-dicyano-1, 2-dimercapto ethene, preferably in solution in an inert solvent or, if desired, in suspension. The corresponding hydroquinone may be prepared by catalytic hydrogenation of the quinone, for example, in dioxane solution using a platinum-carbon catalyst. The compounds may be used as fungicidal agents in fungicidal compositions (see Group VI), paints and lacquers (see Group III) or in the treatment of textiles (see Group VIII). Specification 747,909 is referred to. ALSO: Paints and lacquers comprise, as a fungicide, 2,3-dicyano- 1,4-dithia anthraquinone and/or the corresponding hydroquinone. In an example, a coating composition comprises one or other of these fungicides, chalk, zinc oxide, iron oxide, copper naphthenate, linseed oil, stand oil and a maleate resin worked up in a solvent such as white spirit with or without n-butanol. Specification 747,909 is referred to. ALSO: Fungicidal compositions comprise 2, 3-dicyano-1, 4-dithio anthraquinone and/or the corresponding hydroquinone, and a filler or carrier. The substances are effective against *Rhizoctonia solani*, *Venturia inaequalis* and *Alternaria Spec.*, and may be used in powders, solutions or emulsions for dusting or spraying. Other pest control agents may be added. According to Examples (1) a spraying powder comprises the anthraquinone, kaolin and the sodium salt of the condensation product of oleic acid with methyl taurine, which powder may be sprayed or atomised in the form of a dilute aqueous suspension; (2) an emulsion concentrate comprises the hydroquinone, a specified emulsifying agent, xylene and water; (3) a liquid aerosol comprises the quinone or hydroquinone, methylene chloride, CF<sub>2</sub> Cl<sub>2</sub>, CF Cl<sub>3</sub> and a propanebutane mixture. Specification 747,909 is referred to.

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# PATENT SPECIFICATION

NO DRAWINGS

857,383



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No. 31877/58.

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International Classification:—A01n. C07d. C09d.

## COMPLETE SPECIFICATION

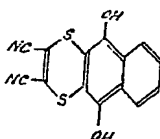
### New Dithia-Anthracene Derivatives and Fungicidal Compositions containing them

We, E. MERCK AKTIENGESELLSCHAFT, of Frankfurter Strasse 250, Darmstadt, Germany, a Germany Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fungicidal agents.

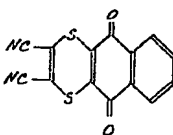
It has been found that 2,3-dicyano-1,4-dithia-anthrahydroquinone of the formula I

I



and the corresponding quinone of the formula

II



have excellent fungicidal properties.

The new compounds have an essentially stronger fungicidal action than the best fungicides obtainable on the market at present.

The fungicidal action of the new compounds has been tested on a great variety of fungi, such as, for example, *Rhizoctonia solani*, *Venturia inaequalis* and *Alternaria Spec.* The average fungicidal action of the new compounds is nearly twice as strong as that of the best commercial products hitherto known such as TMTD (tetramethyl thiuram) disulphide, Captan (N-trichloromethyl-thio-tetrahydrophthal

imide) and Ziram (N,N-dimethyl carbamic acid zinc salt).

The object of the invention is, therefore, to provide a fungicidal composition which contains in addition to a filler or carrier the 2,3-dicyano-1,4-dithia-anthrahydroquinone of the above shown formula I and/or the corresponding quinone of the above shown formula II.

An object of the invention is also the provision of the new compounds themselves.

The fungicides are well tolerated by plants. 2,3-dicyano-1,4-dithia-anthraquinone was worked up, for example, into a 80% spraying powder and used for spraying various vegetable wine and garden plants. None of the treated plants showed any phytotoxicity even when amounts of 1% had been used.

2,3-dicyano-1,4-dithia-anthraquinone can be prepared by reaction of the disodium salt of 1,2-dicyano-1,2-dimercapto ethene, with 2,3-dihalo-1,4-naphthaquinone. 2,3-dichloro-1,4-naphthaquinone is suitably used as the halogen compound. The reaction is expediently carried out in an inert solvent, such as, for example, methanol, ethanol, xylene or acetone. The reaction also proceeds by employing the reagents in suspension instead of solution. 2,3-dicyano-1,4-dithia-anthrahydroquinone can be prepared for example by catalytic hydrogenation of 2,3-dicyano-1,4-dithia-anthraquinone.

Compounds which have a certain similarity in their constitution with the new fungicides are described in U.S. Specification 2,547,723, British Specification 747,909 and German specification 876,018. Comparative tests have shown that these compounds have an essentially smaller fungicidal action than the fungicides according to the present invention.

The new compounds can be worked up in any form of application used for conventional pest control agents. According to known methods spraying liquors or dusting agents can be produced or the compounds can be added to paints or lacquers. In suitable sol-

vents, the compounds according to the invention can also be used for the impregnation of textile fibres. It is also possible to work them up into solutions or emulsions used for spraying according to the aerosol process by applying the usual solvents known for this process. It goes without saying that mixtures of the new fungicides can be employed; the compounds according to the invention can also be used in admixture with other known pest control agents.

In general the preparations contain not more than 95 percent by weight of active substance.

#### EXAMPLES:

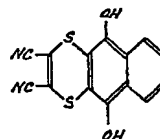
- 15 1. 3.7 g. of the disodium salt of 1,2-dimercapto-1,2-dicyan ethene and 4.6 g. of 2,3-dichloro-naphthoquinone are dissolved in alcohol. The reaction mixture reaches a temperature of about 40° C. by spontaneous heating.
- 20 The reaction is completed by subsequent boiling for half an hour. Cooling to about 10° C. and filtering with suction yield a NaCl-containing crude product. Purification is carried out by leaching with water and recrystallisation from ethylal or acetone. The 2,3-dicyano-1,4-dithia-anthraquinone thus produced crystallises as grey brown needles with a violet metallic lustre and melts at 220° C.
- 25 2. 3 g. of 2,3-dicyano-1,4-dithia-anthraquinone are dissolved in 150 cc. of dioxan and hydrogenated with 2 g. of a platinum-carbon catalyst (10%). Thereupon, the catalyst is filtered off, the filtrate evaporated down, and the residue washed with petroleum ether. The undissolved portion is subsequently recrystallised from acetone. The 2,3-dicyano-1,4-dithia-anthrahydroquinone thus obtained melts upon rapid heating at 215° C.
- 30 Yield 2.9 g.
- 35 3. Spraying powder.  
80 parts of 2,3-dicyano-1,4-dithia-anthraquinone,  
10 parts of kaolin,  
10 parts of the sodium salt of the condensation product from oleic acid and methyl taurine commercial 32%, are ground to give the desired fineness. The powder thus produced can be sprayed or atomized in the form of dilute aqueous suspensions.
- 40 4. Emulsion concentrate.  
40 parts of 2,3-dicyano-1,4-dithia-anthrahydroquinone,  
12 parts of polyoxy ethylene sorbitol ester of a mixture of fatty acids and resinic acids  
45 with a suitable sulphonate, such as commercial calcium dodecyl-benzene-sulphonate,  
3 parts of a sulphonated aliphatic polyester, and  
50 45 parts of xylene are mixed together. The solution thus obtained is emulsified with water and can be sprayed or atomized.
5. Liquid aerosol.

- 24 parts of 2,3-dicyano-1,4-dithia-anthraquinone or 2,3-dicyano-1,4-dithia-anthrahydroquinone, 65
- 76 parts of methylene chloride,  
50 parts of difluoro dichloromethane,  
25 parts of monofluoro trichloromethane and  
25 parts of commercial propane-butane mixture are introduced into an aerosol pressure container for spraying.
6. Coating agent.  
15 parts of 2,3-dicyano-1,4-dithia-anthraquinone or 2,3-dicyano-1,4-dithia-anthrahydroquinone, 75
- 10 parts of chalk,  
8 parts of zinc oxide,  
8 parts of iron oxide,  
5 parts of copper naphthenate, 80
- 8 parts of linseed oil stand oil and  
16 parts of maleate resin are worked up with a total of 30 parts of a solvent to give a coating agent. It is expedient to mix first a small portion of the solvent (e.g. white spirit) with the mixture of ingredients and to add then the remaining portion of the solvent (white spirit with an addition of *n*-butanol, for example). 85

#### WHAT WE CLAIM IS:—

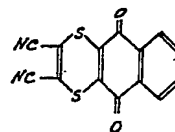
1. A fungicidal composition characterized by containing 2,3-dicyano-1,4-dithia-anthrahydroquinone of the formula I 90

I



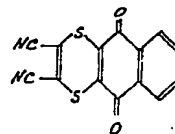
and/or the corresponding quinone of the formula II 95

II

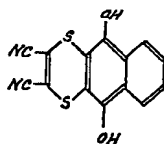


and a filler or carrier.

2. 2,3-dicyano-1,4-dithia-anthraquinone of the formula 100



3, 2,3-dicyano-1,4-dithia-anthrahydroquinone  
of the formula



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